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# Tuning of the excited state properties of phenylenevinylene oligomers: A time-dependent density functional theory study

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# Tuning of the excited state properties of phenylenevinylene oligomers: A time-dependent density functional theory study

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This paper discusses a time-dependent density functional theory study of the effect of molecular structure on the excited state polarizability of conjugated molecules. A short phenylenevinylene oligomer containing three phenyl rings (PV2, distyryl benzene) is taken as a model system. Introduction of methyl substituents is shown to have only a small influence on the increase in polarizability upon excitation (the excess polarizability,  $\Delta\bar{\alpha}$ ). Methoxy groups have a much larger effect but in this case  $\Delta\bar{\alpha}$  depends strongly on the dihedral angle between the side chain and the backbone of the molecule. If the central phenyl ring of PV2 has a *meta*-configuration rather than *para*, both the optical absorption spectrum and the excess polarizability change considerably. © 2003 American Institute of Physics. [DOI: 10.1063/1.1568079]

## I. INTRODUCTION

Conjugated oligomers and polymers are attractive candidates for application in organic optoelectronic devices because of their low cost and easy processability, compared to crystalline inorganic materials. Examples of such devices include light emitting diodes (LEDs),<sup>1,2</sup> solid state lasers, and photovoltaic devices.<sup>3,4</sup> In all of these devices the excited state of the conjugated molecule plays a decisive role. In LEDs the excited electronic state or exciton is formed by combination of an electron and a positive charge (“hole”) that are injected from the opposite electrodes. The excited states decay to the ground state by fluorescence, generally the emission is from the lowest singlet state.

In photovoltaic devices this process is reversed. The first step in this case is light absorption which leads to formation of an exciton. This exciton can dissociate into free electrons and holes which can be collected at different ends of the absorbing material through electrodes. It may be clear that the nature and properties of the electronically excited state of conjugated molecules play an important role in the performance of photovoltaic and light emitting devices.

Valuable information on the nature of excitons in conjugated molecules can be obtained from studies of the changes in the electronic polarizability ( $\Delta\bar{\alpha}$ ) upon excitation. The polarizability of the exciton can be considered as a measure of the spatial extent of the excited state.<sup>5–7</sup> The “size” of the exciton may be one of the factors determining the formation probability of an exciton when an electron and a hole ap-

proach each other. Furthermore, the exciton polarizability is also a measure of the exciton binding energy, the attraction between the electron and hole. A large polarizability, which implies a small exciton binding energy, is favorable for exciton dissociation in photovoltaic devices.

Experimental information on excited state polarizabilities is available from two techniques. The first is the flash photolysis time-resolved microwave conductivity technique (FP-TRMC) in which the change in dielectric constant (i.e., the macroscopic polarizability) upon excitation of molecules in a solution is monitored using microwaves.<sup>5,8</sup> The excited state on which information is obtained is usually the lowest excited singlet state but in materials with an appreciable triplet yield it is also possible to gain information about the triplet state.<sup>9</sup>

The second method is electroabsorption or electroemission spectroscopy,<sup>10,11</sup> where the changes in absorption or emission spectra are monitored as a function of an externally applied electric field. In the case of electroabsorption, information is obtained for the Franck–Condon (vertical) excited state, while in electroemission the relaxed fluorescing state is probed.

The first demonstration of a conjugated-polymer light emitting diode was based on an unsubstituted polyphenylenevinylene (PPV), which is insoluble and thus precludes processing from common organic solvents.<sup>12</sup> Conjugated polymers can be made soluble by the introduction of side chains such as alkyl and alkoxy groups. Introduction of electronically active substituents such as alkoxy or cyano groups also offers the opportunity to tune the absorption and emission wavelength. Substituents can also be expected to

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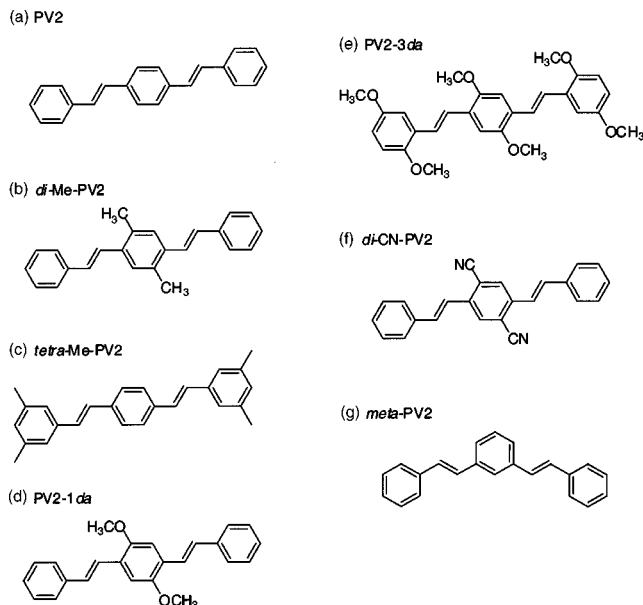


FIG. 1. Structures of the phenylenevinylene derivatives for which calculations have been performed.

have a considerable influence on the electronic properties of the excited state, such as the excited state polarizability. This has been shown experimentally by a FP-TRMC study reported recently by Candeias *et al.*,<sup>13</sup> who showed that the number and position of alkoxy side chains influences the excited state polarizability significantly. Similar observations have been made by Lane *et al.*, who performed electroabsorption measurements.<sup>14</sup>

Recently, it has been shown that the increase in polarizability upon excitation of a molecule (the excess polarizability,  $\Delta\bar{\alpha}$ ) can be obtained by calculating the optical absorption spectrum, using time-dependent density functional theory, as a function of an externally applied electric field.<sup>15</sup> For short conjugated molecules the method was found to give excess polarizabilities that are in good agreement with experimental data. For more extended linear conjugated molecules the excited state polarizability is considerably overestimated, similar to the well-known overestimation of the polarizability of long linear molecules in the ground state.<sup>16,17</sup>

This paper provides a detailed computational study of the effects of substituents and other structural modifications on the excited state polarizability of conjugated molecules. A short phenylenevinylene oligomer, PV2, is used as a model system for PPV, one of the materials that is most often used in polymer-based LEDs and photovoltaic cells. The structures of the molecules that were studied are shown in Fig. 1.

## II. COMPUTATIONAL DETAILS

The calculations described in the following were performed using the time-dependent density functional theory code as implemented in the Amsterdam Density Functional Program Package (ADF).<sup>18–21</sup> The calculations were performed in the same way as published previously for unsubstituted conjugated oligomers.<sup>15</sup> For the ground state calculations the local density approximation for the exchange and

correlation functional based on the parametrization of the electron gas data given by Vosko, Wilk, and Nusair<sup>22</sup> was used, together with the generalized gradient approximation corrections by Becke<sup>23</sup> (exchange) and Perdew<sup>24</sup> (correlation).

The basis set used for the calculations described in the following was of triple zeta quality including polarization functions (TZP, basis set IV in ADF) consisting of Slater-type functions.<sup>25</sup> The geometries of the molecules studied were completely optimized in the ground state, constraining them to  $C_{2h}$  or  $C_{2v}$  symmetry. Excess polarizabilities of these systems were calculated using response theory based on time-dependent density functional theory (TDDFT) as implemented in the RESPONSE code of ADF,<sup>21,26,27</sup> in combination with a static electric field. The combination of TDDFT with a static uniform electric field makes it possible to analyze the electrostatic properties of molecules in their excited state. The dependence of the excitation energy,  $E_{\text{exc}}$ , on a static external electric field depends on the changes in dipole moment and polarizability upon excitation. A change in dipole moment,  $\Delta\mu$ , gives a linear dependence on the applied electric field whereas a change in polarizability,  $\Delta\alpha$ , causes a quadratic field dependence of the excitation energy. For an electric field,  $F_i$ , in direction  $i$ :

$$E_{\text{exc}}(F_i) = E_{\text{exc}}(0) - \Delta\mu_i F_i - \frac{1}{2} \Delta\alpha_{ii} F_i^2, \quad (1)$$

where  $\Delta\alpha_{ii}$  is the change in the  $i$ th diagonal element of the polarizability tensor  $\alpha$ . In the following, the excess polarizabilities are given as average values,  $\Delta\bar{\alpha}$ , defined as

$$\Delta\bar{\alpha} = \frac{1}{3} (\Delta\alpha_{xx} + \Delta\alpha_{yy} + \Delta\alpha_{zz}). \quad (2)$$

The excitation energies for the lowest ten states were calculated for electric fields ranging from 0 to  $3 \times 10^{-4}$  a.u. along all three axes. The largest component of the excess polarizability was found to be the one along the main chain of the molecule. The component directed perpendicular to the plane of the molecule was negligible in all cases.

This method for the calculation of the changes in electrostatic properties is analogous to the way in which excited state properties are obtained from electroabsorption measurements. It was shown previously that the calculated excitation energy indeed varies quadratically with the applied electric field.<sup>15</sup> For short conjugated oligomers the calculated increase in polarizability upon excitation was found to be in good agreement with experimental data. For longer oligomers a large overestimation of the excess polarizability was found, similar to the well-known overestimation of ground state polarizabilities when using conventional exchange correlation functionals.<sup>16,17</sup> Recently Van Faassen *et al.* have demonstrated that this problem of overpolarization can be solved by using so-called current-density-functionals for describing nonlocal exchange-correlation effects in extended conjugated systems.<sup>17,28</sup> It is of considerable interest to examine whether such current-density-functionals also improve the description of the polarizability of the excited state. Such calculations are currently being pursued and will be the subject of a future publication.

The present work is restricted to short oligomers with different molecular structures. It is expected that the overes-

TABLE I. Excitation energy from ground state ( $E_{\text{exc}}$ ), oscillator strength (Osc.), and excess polarizability ( $\Delta\alpha$ ) of PV2 analogues.

Compound	State	$E_{\text{exc}}$ (eV)	Osc.	$\Delta\alpha$ ( $\text{\AA}^3$ )	$\Delta\alpha$ ( $\text{\AA}^3$ ) Expt.
PV2	$^1B_u$	2.67	1.58	351	420 <sup>a</sup>
	$^1A_g$	2.91	0.00	−273	...
diMe-PV2	$^1B_u$	2.69	1.53	271	...
	$^1A_g$	2.97	0.00	−184	...
tetraMe-PV2	$^1B_u$	2.69	1.66	383	300 <sup>b</sup>
	$^1A_g$	2.96	0.00	−274	...
PV2-1da	$^1B_u$	2.47	1.04	91	150, <sup>b</sup> 340 <sup>a</sup>
	$^1A_g$	2.90	0.00	362	
	$^1B_u$	2.96	0.52	−301	
PV2-3da	$^1B_u$	2.22	1.06	808	311 <sup>a</sup>
	$^1A_g$	2.35	0.00	−620	...
PV2-CN	$^1B_u$	2.52	0.52	107	...
	$^1B_u$	2.72	1.00	283	
	$^1A_g$	2.89	0.00	−229	
meta-PV2	$^1B_2$	2.83	0.03	1148	...
	$^1A_1$	2.92	0.05	−1084	...
	$^1B_2$	3.51	1.80	88	80 <sup>a</sup>

<sup>a</sup>Experimental data from electroabsorption measurements by Lane *et al.* (Ref. 14).

<sup>b</sup>Experimental data from FP-TRMC measurements by Gelinck *et al.* (Ref. 5).

timination of the polarizability is of minor importance in this case since a good agreement with experimental data was obtained previously for molecules of similar size.<sup>15</sup> Moreover, the main focus in this work is on the effect of substituents on the excess polarizability rather than on the absolute magnitude.

### III. RESULTS AND DISCUSSION

Calculations of the excess polarizability were performed for all structures shown in Fig. 1 by the method outlined in Sec II. Table I gives the results obtained for selected excited states of the molecules studied. The results for PV2 from Ref. 15 are also given for comparison with the substituted analogues of PV2. Table I also gives experimental values where these are available.

#### A. Methyl substituents

The first type of substituent considered here are methyl groups, see structures (b) and (c) in Fig. 1. The results for methyl substituents can be considered representative for the effect of alkyl side chains on the properties of excitons. Conjugated polymers are often substituted with alkyl chains in order to make them (more) soluble. Introduction of two methyl groups on the central phenyl ring of PV2 with  $C_{2h}$  symmetry, giving *di*-Me-PV2, hardly influences excitation energy and oscillator strength of the lowest allowed absorption band. The calculated excess polarizability of the lowest  $^1B_u$  state, 271  $\text{\AA}^3$ , is somewhat ( $\sim 20\%$ ) lower than that for the unsubstituted PV2, 351  $\text{\AA}^3$ . This decrease in excess polarizability can be related to the energy difference between the lowest  $^1B_u$  state and the next  $^1A_g$  state. The polarizability,  $\alpha_a$ , for state  $a$  in terms of the sum-over-states expression is given by<sup>29</sup>

$$\alpha_a = \frac{2}{3} \sum_{n \neq a} \frac{|\mu_{na}|^2}{\Delta E_{na}}. \quad (3)$$

In Eq. (3) the summation runs over all states other than  $a$ .  $\Delta E_{na}$  is the energy difference between states  $a$  and  $n$  and  $\mu_{na}$  is the transition dipole moment between these states. In this description, the polarizability of a  $^1B_u$  exciton is due to mixing with all other  $^1A_g$  states, since these are the only states for which  $\mu_{na}$  is nonzero in  $C_{2h}$  symmetry. The main contribution to the polarizability of the lowest  $^1B_u$  state is in general due to the next higher  $^1A_g$  state since the energy difference,  $\Delta E_{na}$ , in the denominator is the smallest for this contribution. This same interaction leads to a negative value for  $\Delta\alpha$  for the lowest  $^1A_g$  state that is of similar magnitude as the positive value for the lowest  $^1B_u$  state, as discussed previously.<sup>15</sup> The difference in excess polarizability for the lowest  $^1B_u$  excited state for *di*-Me-PV2 and PV2 can now be explained by considering the energy difference between the lowest  $^1A_g$  and  $^1B_u$  excited states. This energy difference is somewhat larger for *di*-Me-PV2, causing a decrease in the exciton polarizability.

Alternatively, the differences in excess polarizability can be discussed in a more qualitative way in terms of the degree of delocalization or the “size” of the exciton. The methyl groups at the central phenyl ring have a localizing effects on the exciton because the energy of an exciton localized on the substituted phenyl ring is lower than that for an unsubstituted phenyl ring. The (fractional) localization of the exciton is reflected in a smaller excess polarizability.

The second methyl-substituted oligomer, *tetra*-Me-PV2 [Fig. 1(c)], has two methyl groups on the terminal phenyl rings. The excess polarizability for this molecule (383  $\text{\AA}^3$ ) was calculated to be somewhat larger than that for the unsubstituted PV2. If the energy difference between the lowest  $^1B_u$  and  $^1A_g$  excited states is compared to that for PV2 in this case, it is found that there is not much difference, the value for *tetra*-Me-PV2 is even somewhat larger. This clearly indicates, that although the largest contribution is due to mixing with the lowest  $^1A_g$  state above the  $^1B_u$  state, the mixing with other states is also important for explaining subtle differences between the excess polarizabilities for *tetra*-Me-PV2 and PV2.

In terms of the degree of delocalization of the exciton it can be said that the methyl groups on the terminal phenyl rings lower the exciton energy at these sites, causing a more delocalized exciton, and consequently a higher excess polarizability.

An experimental value for the excess polarizability is available for PV2 from electroabsorption measurements (420  $\text{\AA}^3$ ).<sup>14</sup> From FP-TRMC experiments an excess polarizability was measured for a PV2 that has two tertiary butyl groups on both the outer rings, analogous to *tetra*-Me-PV2 in Fig. 1. From these measurements a value of 300  $\text{\AA}^3$  was obtained.<sup>5</sup> These two experimental values cannot be compared directly because of considerable differences between both experiments. In the electroabsorption measurements the vertical excited state of a molecule trapped in a solid matrix is probed while in the FP-TRMC technique the relaxed excited state is studied in dilute solution. Because of these dif-



ferences, it is difficult to derive the actual effect of the introduction of methyl substituents from the experimental data. It is concluded that the calculated excess polarizabilities for both *tetra*-Me-PV2 and PV2 are in reasonable agreement with the experimental values available.

## B. Methoxy substituents

Most poly- and oligo-phenylenevinyls that are used in experimental work are substituted with solubilizing alkoxy side chains. It was shown recently in a computational study that alkoxy groups have a large influence on the degree of delocalization of a positive charge along a phenylenevinylene chain.<sup>30</sup> A similar effect is obtained for the lowest excited  ${}^1B_u$  state of PV2. Introduction of two methoxy substituents on the central ring, giving PV2-1 *da* [Fig. 1(d)], lowers the excess polarizability from 351 Å<sup>3</sup> (PV2) to only 91 Å<sup>3</sup>. Alkoxy side chains have much stronger localizing effects than the above-discussed alkyl groups. This indicates that atomic orbitals on the oxygen atoms of the methoxy groups contribute significantly to the  $\pi$ -electron system of the phenylenevinylene backbone. If the energy difference between the lowest excited state (of  ${}^1B_u$  symmetry) and the second excited state for PV2-1 *da* is compared to that energy difference for PV2 it is clear that the introduction of two methoxy substituents on the central phenyl ring considerably increases the energy difference. According to the sum-over-states description in Eq. (3) this increase in the energy difference leads to a considerable lowering of the polarizability of the excited state of PV2-1 *da* compared to that for PV2. Note, that in the case of PV2-1 *da* the lowest  ${}^1A_g$  state has a positive excess polarizability. This can be understood by considering the next  ${}^1B_u$  state, included in Table I. The energy difference between the lowest  ${}^1A_g$  excited state and the second  ${}^1B_u$  excited state is very small (0.06 eV), which leads to a large positive contribution due to the mixing between these states [see Eq. (3)] to the polarizability of the lowest  ${}^1A_g$  excited state. Thus the excess polarizability of the lowest  ${}^1A_g$  excited state is dominated by mixing with the higher lying  ${}^1B_u$  state rather than with the lower lying  ${}^1B_u$ .

From experimental work there are two sets of data. The first are from electroabsorption measurements where the excess polarizability decreases from 420 Å<sup>3</sup> for PV2 to 340 Å<sup>3</sup> for PV2-1 *da*, a decrease of only 20%.<sup>14</sup> From FP-TRMC measurements a considerably larger decrease from 300 Å<sup>3</sup> for *tetra*-*t*-butyl-PV2 to 150 Å<sup>3</sup> for PV2-1 *da* was obtained.<sup>5</sup> The large differences between these experimental values and the trends in them may be caused by differences in the surrounding medium. In the electroabsorption measurements by Lane *et al.*,<sup>14</sup> measurements were performed in a solid PMMA matrix at 77 K, whereas in the FP-TRMC experiments by Gelinck *et al.* the oligomers were studied in benzene solution at room temperature.<sup>5</sup> These very different environments can cause considerable differences in the geometry of the PV oligomer. Another source of the differences can be a more fundamental difference between FP-TRMC and electroabsorption. In electroabsorption it is the vertical (Franck-Condon) excited state that is probed, which means that the excess polarizability that is obtained is the difference between the ground state polarizability (in the ground state

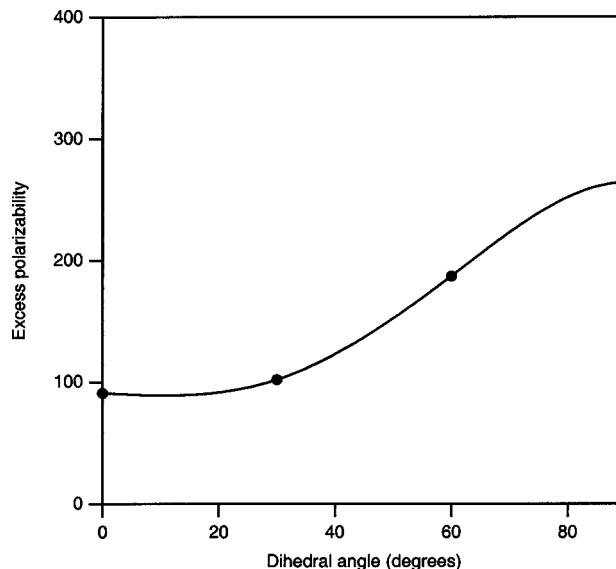


FIG. 2. Dependence of the excess polarizability for the lowest  ${}^1B_u$  excited state in PV2-1 *da* on the dihedral angle between the methoxy side chains and the plane of the conjugated backbone.

geometry) and the excited state polarizability in the *ground state geometry*. In contrast FP-TRMC measurements are performed on the relaxed excited state. If there are large differences between the ground state and excited state geometries the results from both techniques may exhibit considerable differences. Conformational differences may also be a source of differences between calculated and experimental values.

One of the structural changes that can affect the excess polarizability is the dihedral angle between the PV backbone and the methoxy side chain. In all calculations presented in Table I for methoxy substituted PVs the carbon atoms in the methoxy groups are in the plane of the PV backbone, defined here as the dihedral angle equal to zero. Figure 2 shows the dependence of the excess polarizability for PV2-1 *da* on the dihedral angle between the PV backbone and the methoxy side chain (the rotation is around the bond between the backbone C atom and the methoxy O atom). The excess polarizability is minimal (91 Å<sup>3</sup>) for an angle equal to zero and increases up to 264 Å<sup>3</sup> for the geometry where both side chains are perpendicular to the PV plane. This indicates that there is indeed a strong mixing between the  $\pi$ -electron system on the PV backbone and a  $\pi$ -type orbital on the oxygen of the methoxy group. Inspection of the highest occupied and lowest unoccupied Kohn-Sham orbitals for a zero dihedral angle revealed that there is indeed a *p*-type orbital on the methoxy groups that contributes to this orbital. The mixing of the  $\pi$  orbitals on the methoxy group and the PV backbone depends strongly on the dihedral angle, as reflected in the excess polarizability. Other geometry deformations that may affect the excess polarizability are rotations around bonds in the PV backbone. Such rotations will decrease the electronic coupling along the backbone and are therefore expected to lower the excess polarizability.

The second alkoxy substituted PV2 in Table I, PV2-3 *da* [Fig. 1(e)], contains two methoxy substituents on all phenyl rings. The excess polarizability for the lowest  ${}^1B_u$  state in

PV2-3 *da* was calculated to be  $808 \text{ \AA}^3$ . This is much larger than the experimental value from electroabsorption measurements ( $311 \text{ \AA}^3$ ).<sup>14</sup> Furthermore, the calculated trend in the excess polarizability for the series PV2, PV2-1 *da*, and PV2-3 *da* differs considerably from the results from electroabsorption measurements. The calculations show that introduction of two methoxy groups on the central phenyl ring localizes the exciton. When all phenyl ring are di-alkoxy substituted the excess polarizability becomes larger again, even considerably larger than for the unsubstituted PV2.

In the electroabsorption experiments the introduction of alkoxy side chains on all phenyl rings does not recover the excess polarizability, in fact it was found that it is lowered even more. It is not unlikely that this is caused by geometry deformations in the case of the experiment since the compounds used contain rather long (decyl) side chains. Steric interactions between these chains may force geometry deformations to occur.

FP-TRMC experiments have been performed for an analogous series of PVs containing five phenyl rings.<sup>13</sup> It was found that introduction of two alkoxy groups on the central phenyl ring reduces the excess polarizability by  $\sim 30\%$ . When all phenyl rings are dialkoxy substituted, the exciton was completely delocalized again and the excess polarizability was even slightly higher than for the unsubstituted oligomer. These FP-TRMC data qualitatively follow the calculated trends in the excess polarizability for oligomers containing three phenyl rings as considered here.

The comparison of experimental data with calculations is somewhat difficult for oligomers that are substituted with rather flexible alkoxy side chains. The exact nature of the side chains may also play a role here. In the calculations a methoxy substituent is taken, whereas experiments have been performed with considerably longer (branched) alkoxy chains. The electronic effect of these longer side chains is expected to be similar to that for a methoxy group. There may, however, be effects due to steric interaction between side chains on different units that cause structural changes. In the case of alkoxy substituted PV oligomers there are already considerable (quantitative and qualitative) differences between experimental results from different methods, which makes it rather difficult to establish the accuracy of the computational method used for these cases. It should be noted that this is especially the case for oligomers containing flexible alkoxy side chains. For relatively rigid molecules such as unsubstituted or methyl-substituted PVs there is a very reasonable agreement between experimental data from different techniques and with the calculated values presented here. The same is true for *meta*-PV2, discussed in the following.

### C. Cyano substituents

The third type of substituents considered here are cyano groups. The calculated excess polarizability for CN-PV2 [Fig. 1(f)], containing two cyano groups on the central phenyl ring, was found to be  $107 \text{ \AA}^3$  for the lowest  $^1B_u$  state. This shows that cyano groups have a similar exciton-localizing effect as alkoxy side chains. There is a strong cou-

pling between orbitals on the cyano groups and the  $\pi$  system of the PV backbone. This also causes a second allowed transition (to a  $^1B_u$  state) to appear, 0.2 eV above the lowest, with an excess polarizability of  $283 \text{ \AA}^3$ . The higher polarizability of this second  $^1B_u$  state can easily be related to the lower energy difference with the higher lying  $^1A_g$  state.

There is no experimental information for the cyano substituted PV2 considered here. FP-TRMC experiments have been performed on a PV oligomer of five phenyl rings that contained, apart from alkoxy chains on the central ring, a single cyano group on each of the vinyl moieties neighboring the central ring.<sup>13</sup> It was found that the presence of these two cyano groups considerably lowers the excess polarizability, in agreement with the calculations presented here.

### D. Meta-PV2

Finally, a PV2 oligomer is discussed that has a backbone that differs from the standard PV2 structure, rather than modifications in the side chains. In *meta*-PV2 the two styryl groups are connected to the central ring in a *meta*-configuration rather than the *para*-configuration leading to  $C_{2v}$  symmetry rather than  $C_{2h}$  [see Fig. 1(g)]. In contrast to the situation for all other PV2 derivatives considered in this work the calculations show that the transition to the lowest excited state is only weakly allowed. The first strongly allowed transition, with an oscillator strength of 1.8, was found to be due to an excitation to the third excited state. Table I gives the excess polarizability for the lowest three excited states of *meta*-PV2. The lowest excited state, of  $^1B_2$  symmetry, has a very large excess polarizability ( $1148 \text{ \AA}^3$ ) compared to that for PV2. This large value can be attributed to mixing with the next, close lying, excited state of  $^1A_1$  symmetry to which a strongly allowed transition is expected to exist. Accordingly, the second excited state has a negative excess polarizability of similar absolute magnitude, which indicates that the excess polarizabilities of these two states are mainly determined by mutual coupling between them. For the third excited state, which dominates the absorption spectrum of *meta*-PV2, the calculated excess polarizability is rather low ( $88 \text{ \AA}^3$ ) compared to that for PV2. This value can be compared to experimental data from electroabsorption measurements,<sup>14</sup> since in this technique the excess polarizability of excited states to which allowed transition exists is probed. An experimental value of  $80 \text{ \AA}^3$  was obtained from such measurements by Lane *et al.*,<sup>14</sup> which is in good agreement with the calculated value. It would be of interest to perform FP-TRMC measurements on *meta*-PV2 since in this technique the lowest (electrically and vibrationally) relaxed excited state is probed. This would make it possible to establish whether there is indeed a lower lying excited state with a high excess polarizability as predicted by the calculations presented here.

## IV. SUMMARY AND CONCLUSIONS

This paper discusses a time-dependent density functional theory study of the effect of structural modifications on the excited state polarizability of conjugated molecules. A short phenylenevinylene oligomer containing three phenyl rings

(distyrylbenzene, PV2) is taken as a model system. Introduction of alkyl substituents (methyl) was found to have only a small effect on the excess polarizability. If methyl groups are present only on the central phenyl ring the excess polarizability is slightly reduced compared to that for the unsubstituted PV2, which indicates that the presence of methyl groups slightly localizes the exciton. If the outer rings are methyl-substituted there is a slight increase in excess polarizability.

Introduction of alkoxy (methoxy) side chains has a much larger effect on the excess polarizability. If two methoxy groups are present on the central phenyl ring the excess polarizability is strongly reduced. This reduction depends on the dihedral angle between the methoxy group and the PV backbone. The maximum reduction (a factor of 4) is reached if the methoxy-carbon atom is in the same plane as the backbone. If all phenyl rings are dialkoxy substituted the excess polarizability increases again, to a value even higher than for the unsubstituted oligomer. Cyano substituents were found to have a similar localizing effect on the excited state as methoxy groups.

If the central phenyl ring is connected to the outer styryl moieties in a *meta*-configuration rather than *para*, the properties and nature of the excited states change considerably. A low-lying excited state to which only a weak optical transition exists was found with a much larger excess polarizability than that of PV2. A higher lying state to which a strongly allowed transition exists was found to have a much lower excess polarizability.

The calculated values for relatively rigid oligomers (PV2, Me-PV2s, and meta-PV2) were found to be in good agreement with the experimental data available. For molecules containing more flexible groups (e.g., methoxy) the comparison with experimental data is more difficult since conformational changes can have a large effect on the excess polarizability. In these cases there are also significant differences between experimental data from different techniques. It was found, however, that the qualitative trends in the experimental data are reproduced in most cases.

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